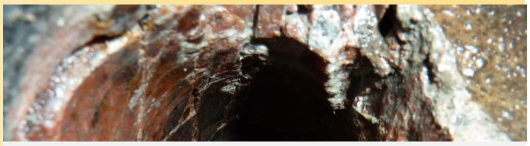
Issue 3, June 2013

Newsletter CROCK (Crystalline ROCK retention processes) project



Content

Further information can be found at the CROCK website:

www.crockproject.eu

Newsletter submitting organization:

Amphos 21
Passeig Garcia i Fària 49-51
E08019 Barcelona,

Dear readers,

We are pleased to present the third and last Newsletter of the Collaborative project CROCK. This publication aims to inform you on the main results and advances accomplished within the different work-packages and, about the final overall output of the project.

CP CROCK was born to decrease the high uncertainty and the associated conservatism with respect to the radionuclide transport predictions in the crystalline host-rock far-field around a geological disposal of high-level radioactive wastes. The CP CROCK is formed by a team of professionals from multiple disciplines which allow the project to be undertaken in different areas (chemistry, geology, hydrogeology, geochemistry, physics, etc.) and on different scales (macro, micro and nano).

National Waste Management Organizations participate in the project contributing with co-funding to beneficiaries, infrastructures, knowledge and sharing information. They also participate together with National Regulators to guidance with respect to application of the project to the disposal Safety Case. For a more concise description of the project origins and objectives the reader is referred to the project website.

After 30 months our project is coming to the end. We wish to extend our greatest thanks to each and everyone of you who contributed to the fulfilment of CROCK's objectives and to creating such pleasant working atmosphere.

Enjoy the reading!

The Coordination Team

WP leader:

Thomas Rabung

KIT-INE

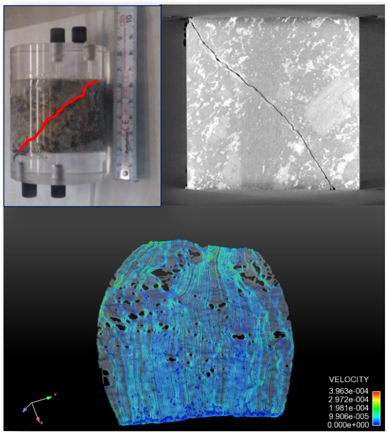
WP1: Experimental material and characterization

The organization and characterization of new crystalline rock samples from Äspö, as well as ensuring the access to experimental samples from previous studies, were the main objectives within this WorkPackage (WP). Five organizations actively worked in this WP: KIT-INE (Germany), CIEMAT (Spain), HZDR (Germany), CTH (Sweden) and MSU (Russia). The work of this workpackage started on January 2011 and finished after 24 months.

Two Deliverables, D1.1 and D1.2, were generated in the frame of this WP compiling main WP achievements / activities. Besides Deliverables, several Scientific & Technical (S&T) contributions were presented in both, the 1st and the Final Workshop of the project, detailing the work done. Below, a brief summary of the overall WP performance is provided.

First activities consisted in organizing new samples of fractured and intact crystalline rock drill cores (sampled under anoxic conditions) and natural groundwaters from Äspö (Sweden). All samples were directly transferred to KIT-INE and stored under Ar atmosphere. A detailed characterization of the sampled materials (including X-Ray Fluorescence Spectroscopy, SEM-EDX (Scanning Electron Microcopy with Energy-dispersive X-ray spectroscopy), XPS (X-Ray Photoelectron Spectroscopy) and N_2-BET measurements of specific surface area) was reported by Holgersson (2012, 2013) and Schäfer et al. (2012) in the proceedings of the CP CROCK Workshop.

Detail of sampling campaign



Different views of the rendered fracture geometry as obtained by the CT dataset.

Additionally, Deliverable D1.2: “Characterization of experimental material”, included the latest Äspö sample characterizations based on Computed Tomography (CT) techniques (left figure). This technique provided valuable geometrical information on the fractures.

Biofilms sampling and characterization (EF-TEM (Energy-Filtered Transmission Electron Microscopy), EELS (Electron Energy Loss Spectroscopy), ICP-MS (Inductively Coupled Plasma Mass Spectrometry), XRD) of site specific biofilms from Äspö HRL was also performed in WP1. Details of this characterization can be found in Krawczyk-Bärsch et al. 2013 included in the Final CROCK Workshop proceedings.

Picture of biofilms in Äspö HRL environment

WP leader:

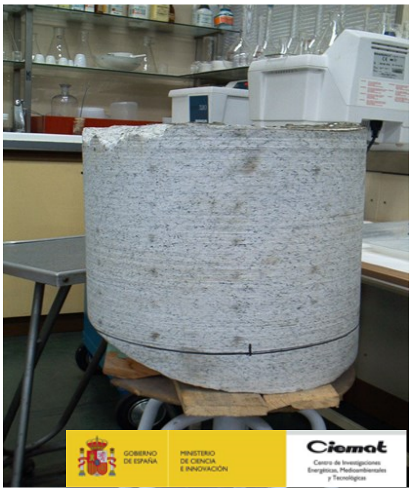
Thomas Rabung

KIT-INE

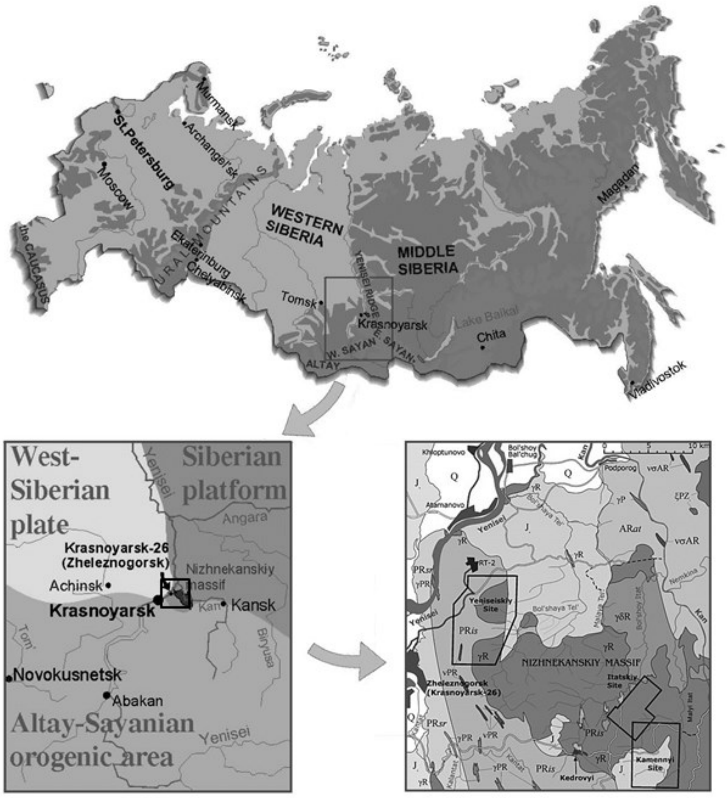
WP1: Experimental material and characterization

In the other hand, two organizations focused their work on two additional granitic materials: a previous material coming from the "block-scale" experiments designed for the FP6-FUNMIG project (CIEMAT), and several Russian rock samples from proposed areas for holding the future HLW and SNF Russian repository (MSU).

An update of sorption data for three different tracers (HTO, $^{36}Cl^-$, $^{137}Cs^+$) on "block-scale" material was obtained by CIEMAT within this WP. The used material was Grimsel (Switzerland) granite from the FEBEX tunnel. Compacted bentonite was also used in the configuration of the experiments. Moreover, a comparison of sorption properties of granites from different origin (Spain, Switzerland, Finland and Sweden) was done.

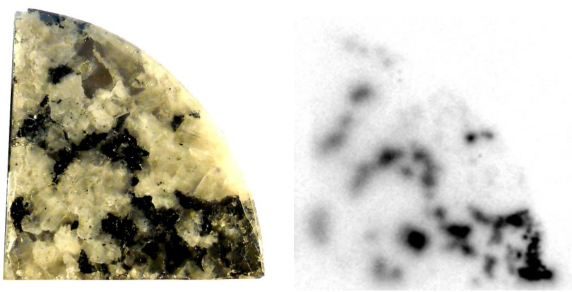


"Block-scale" material picture



Source: Jardine et al. (2005)

Granites from Kamenny and Itatsky areas (Nizhnekansky massive, Russia) were analyzed and characterized by MSU through autoradiography, SEM-EDX and profilometry techniques. A complete petrographic description of the samples was provided and can be found in the S&T contribution by Petrov et al. 2012 in the 1st Workshop Proceedings.



An example of granite slice (Kamenny, 702 m) – on the left, and radiography image of Cs sorption on its surface – on the right.

WP leader:

Tiziana Missana

CIEMAT

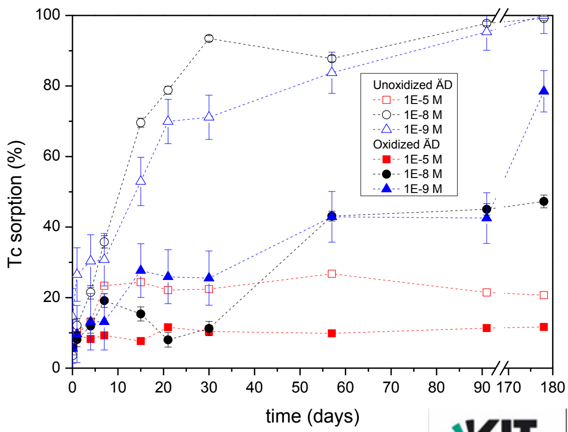
WP2: Radionuclide transport and sorption studies

The main objective of WP2 was to decrease the degree of uncertainty on retention parameters in crystalline rocks by providing sound experimental methodologies and improving the knowledge on retention processes in such heterogeneous materials.

This workpackage lasted 21 months, finishing last March 2013. Six organizations worked within this workpackage: CIEMAT (Spain), KIT-INE (Germany), HZDR (Germany), NRI (Czech Republic), MSU (Russia) and CTH (Sweden).

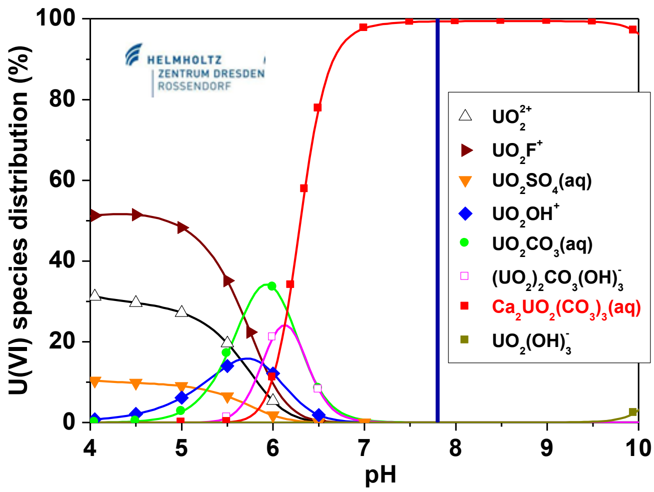
Studies were focused on several granites and granitic minerals from different sites (Spain, Sweden, Switzerland, Russia), with a special emphasis was made on Äspö diorite. The following radionuclides were studied within this workpackage: an ion-exchangeable dominated (Cs) element, a strongly sorbing surface complexation dominated element (Eu), redox sensitive elements (U, Np, Tc, Se) and conservative non-sorbing tracers (HTO, Cl), as agreed by all the partners at the CROCK kick-off meeting. In the following a few details of the work done by each organization is summarized, the complete description of the works could be found in the proceedings of the 1st and Final CP CROCK Workshop.

KIT-INE focused on the study of sorption and desorption of radionuclides. In particular, they studied the sorption/ desorption of $^{137}Cs(I)$, $^{152}Eu(III)$, $^{233}U(VI)$ and Tc(VII) onto Äspö diorite (from the sampling campaign performed in WP1) and Nizhnekansk granite from Russia. In addition, Tc sorption onto magnetite was studied. The details of these activities are detailed in the S&T contributions Stage et al. (2012), Totskiy et al. (2012, 2013) in the proceedings of the 1st and Final CP CROCK Workshop.



% Tc(VII) sorption onto Äspö diorite in function of time.

The determination of the retention behaviour of diorite from the Äspö Hard Rock Laboratory (HRL, Sweden) towards U(VI) and Np(V) under anoxic conditions was done by **HZDR** as a function of: a) contact time, and b) U(VI) concentration. Specifically their objective was to obtain distribution coefficients for those elements under anoxic conditions. A detailed description of these activities is provided in the S&T contributions Schmeide et al. (2012, 2013).



Uranium(VI) speciation in Äspö groundwater ($[U]_{total}$ = 1´10^{-6} M, N_2).

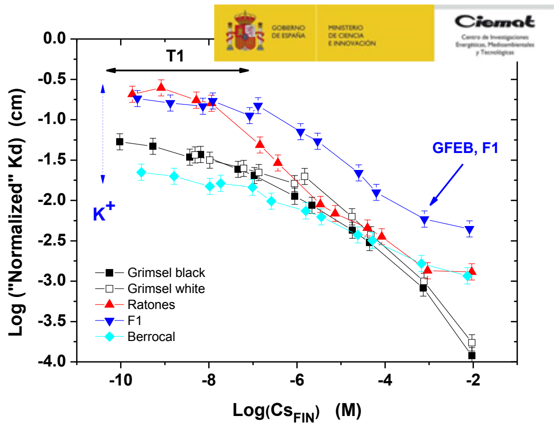
WP leader:

Tiziana Missana

CIEMAT

WP2: Radionuclide transport and sorption studies

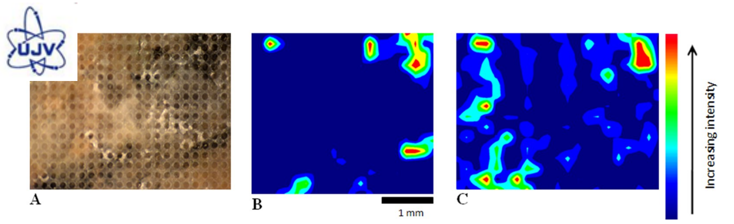
CIEMAT aims to determine sorption of U(VI), Tc(VII) and Eu(III) onto different granitic materials (granites of different origin, biotite and muscovite) under experimental conditions as similar as possible to reduce the experimental uncertainties. Sorption data were analyzed (radio-analytical, mPIXE, RBS autoradiography, SEM-EDAX) to evidence all the possible differences (mineral content, BET area, chemistry of the water, competitive ions in solution, radionuclide concentration, etc.,). The S&T contributions Missana and García-Gutiérrez (2012) and Missana et al. (2013) included a detailed characterization of these works.



Cesium isotherms in different granites. Kd data normalized to the BET surface area

CTH studied sorption of Cs, Ra and U on some sections in the middle of an Äspö drill core sample. However due to some experimental shortcomings their diffusion and sorption experiments were delayed about 3 months and results will be available on September 2013. Sorption experiments with Se(IV) and Se(VI) on Äspö rock samples in Äspö groundwater were performed under aerobic and anaerobic conditions by **UJV**. Se distribution and oxidation state in the rock surface was investigated through the use of ICP-LA and ESCA techniques. Potential anion exclusion in Äspö diorite was also studied by **UJV** through electromigration experiments using ^{3}H (tracer) and ^{36}Cl (anionic species). More details of these work can be found in the S&T contributions Videnska et al. (2012, 2013a, 2013b) Vercernik et al. (2012, 2013).

MSU focused on sorption experiments of Cs, U and Eu onto granitic materials from Kameny and Nizhnekansky areas (Russia) accompanied by various spectroscopic investigations with micro- to nano-resolution and bulk scale. Detailed information can be found in S&T contribution Kuzmenkova et al. (2013).



LA-ICP-MS map of diorite surface after contact with [Na_2SeO_3]=2·10^{-3} M. A) analyzed surface, B) iron distribution, C) selenium distribution

Main outcome gathered from WP2 is briefly summarized as bullet points in below:

- K_d values for different radionuclides in a wide range of experimental conditions has been obtained.
- Retention processes have been analyzed at a mineral scale with different surface techniques.
- Transport parameters for ^{3}H, ^{36}Cl were obtained by diffusion experiments. D_e and F_f for Äspö diorite samples with different lengths were obtained by electromigration.
- Results demonstrated that experimental (and conceptual) uncertainties on transport can be evaluated.
- The use of “well-preserved” materials clearly increases the retention of redox-sensitive elements, most probably due to their surface reduction. The presence of Fe(II) in the rocks is very important in triggering surface reduction.

WP leader:

John Smellie

CONTERRA AB

WP3: Real system analysis

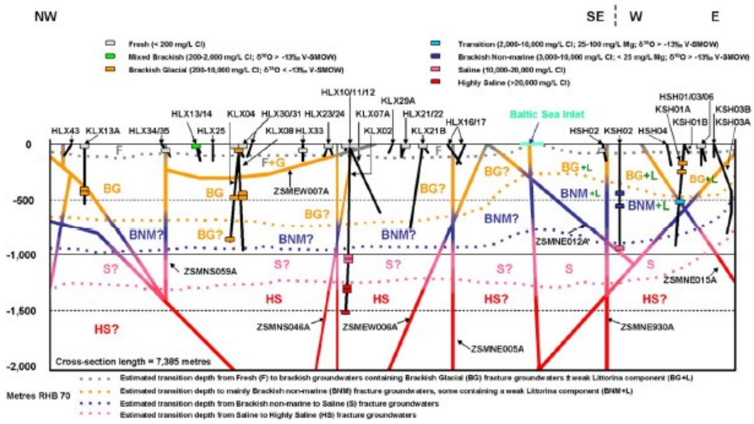
The main objective in WP 3 was to supply all relevant background sources of the analytical and field pore water data (together with interpretations) from the recent Swedish site characterisation programme with a focus on matrix diffusion. All data provided were from the Forsmark and Laxemar sites with the majority collected from the period 2003-2008. Some additional data from Forsmark were taken more recently in 2011. Three organizations, CONTERRA (Sweden), KEMAKTA (Sweden) and Amphos 21 (Spain), were working in WP3.

Two Deliverables 3.1 and 3.2, and their subsequent updates, were generated in this WP summarising all the information gathered from the works done by beneficiaries. Moreover three S&T contributions (Crawford, 2012; Smellie, 2012, 2013) were published in the Proceedings of the 1st and/or Final project Workshop (Rabung et al., 2012, 2013).

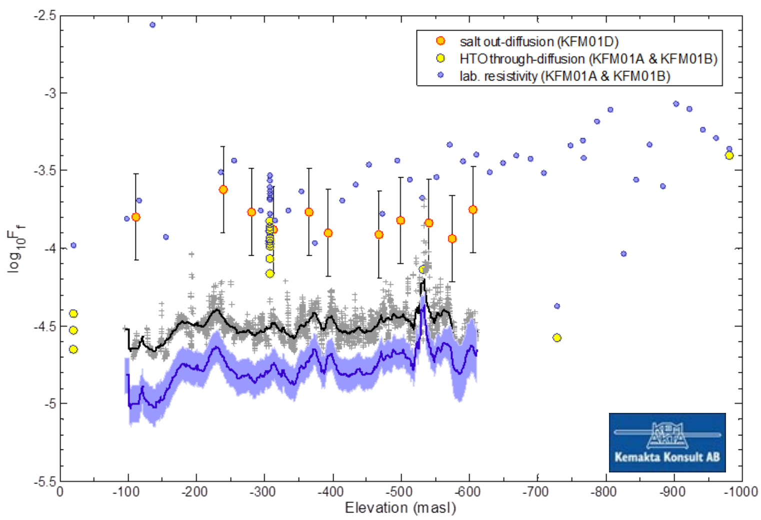
In the S&T contributions by Smellie (2012, 2013) a detailed description of the data supplied to the project beneficiaries is well documented.

Additionally, since porewater ionic strength measurements are uncertain and frequently too low to be able to discount this effect, a significant bias can be introduced which may result in overestimations when interpreting data obtained using *in-situ* geophysical technique. Thus an improved method for correcting the data measurement to remove the theoretical bias introduced by surface conduction has been derived. The method is based on the use of an empirical power law relation describing how surface conduction varies as a function of the true geometric formation factor as ascertained in independent laboratory experiments made using core samples saturated with water of differing ionic strengths. Additional details can of this work can be found in the S&T contribution Crawford (2012).

Is worth to mention that Information about diffusion length, porosity and diffusion coefficients derived from field data in WP3, have been later on incorporated in quantitative models of Workpackage 5.



Approximately NW-SE/W-E cross section through the Laxemar-Simpevarp area (Smellie, 2012).



Best estimate geometric formation factor (log_{10} values) as a function of borehole elevation for rock surrounding Forsmark borehole KFM01D as determined by the in-situ measurement technique shown as a 10m running average

WP4: Conceptualization and modeling

WP leader:

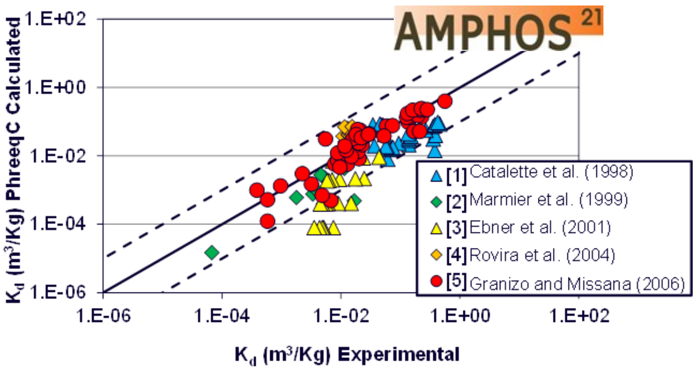
James Crawford

KEMAKTA

The general objective of this WP has been to conceptualize and model radionuclide transport processes on different systems at different scales, thereby decreasing the Performance Assessment (PA) uncertainty and providing improvements for future site characterizations.

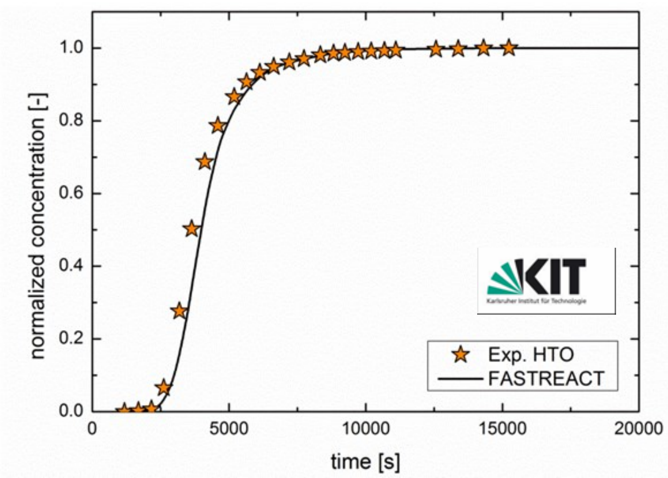
KEMAKTA was leading this WP, where three additional organizations were involved: Amphos 21 (Spain), KIT-INE (Germany) and VTT (Finnland). One deliverable D4.1 and its update was prepared in the frame of this WP as well as several S&T contributions (Crawford, 2012, 2013; García et al., 2013; Huber et al., 2013; Itälä et al., 2013, Olin et al., 2012) published in the 1st and/or Final Workshop Proceedings (Rabung et al., 2012, 2013).

Different systems have been studied and modeled within this WP: Ni(II) and Eu(II) sorption onto biotite; Cs(I), and Eu(III) sorption onto magnetite, illite and iron-hydroxides phases; Np(V) transport in a fracture of Äspö. In addition, the application of linear free energy relationships (LFER) to overcoming the scarcity of experimental data for surface complexation modeling in the boot-strapped component additivity approach was explored.



Experimental K_d values for the Cs-magnetite system vs values calculated with PhreeqC using the model of Granizo and Missana (2006).

Below, few details are provided of the main WP4 activities. A spreadsheet-based surface complexation and cation-exchange model for deriving K_d values for specific water phase conditions (pH, ionic strength, dissolved ligand concentrations etc.) and rock properties (amount of mineral in the host rock, porosity and density) was evaluated for Cs(I) and Eu(III) sorption over magnetite, illite and iron-hydroxides phases. Detailed explanations can be found elsewhere (Garcia et al., 2013).



Simulated HTO breakthrough curve by FASTREACT using the fitted PDF in comparison to the cumulative experimental HTO breakthrough curve (orange stars).

FASTREACT approach has been coupled to PHREEQC in an attempt to describe Np transport through a fractured drill core from the Äspö Hard Rock Laboratory. The model was able to fit the breakthrough time of the Np elution reasonably well, but not the peak concentration nor the pronounced tailing in the elution profile. In the S&T Huber et al. (2013) a complete work description is provided.

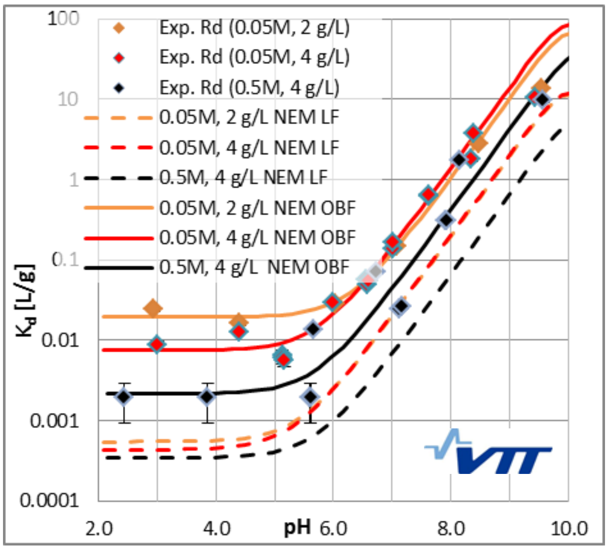
WP leader:

James Crawford

KEMAKTA

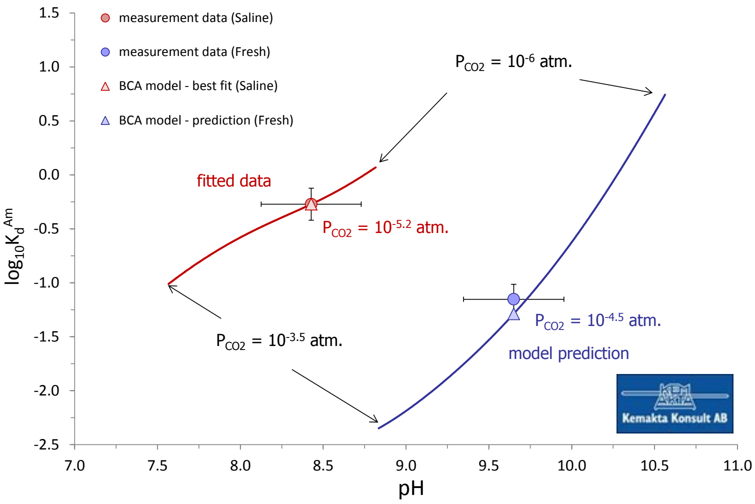
WP4: Conceptualization and modeling

Biotite is an important reactive mineral phase as was e.g. evidenced for the Finnish Olkiluoto repository site. Quantum chemical approaches together with three surface complexation models (non electrostatic, diffuse layer and constant capacitance) were tested for their ability to fit Ni and Eu sorption data into 3 biotite and 2 rock samples (Ni only) over a pH range of 2-10. It was concluded that, the non-electrostatic model gave better fits to the data than the diffuse layer or constant capacitance models, and it was able to model Ni better than Eu, due to the very high Eu sorption observed at high pH. For additional details the reader is referred to the S&T contribution Itälä et al. (2013).



K_d fits for nickel on Olkiluoto B biotite (OBB) 2-4 g/L, 0.05-0.5M.

Boot-strapped component additivity model (BCA) predictions of K_d for Am on Forsmark metagranite in contact with the Fresh groundwater (blue triangular markers) as compared with measured values (blue circular markers).



LFER application assumed that the binding constants of dissolved metals to a mineral phase show a linear relationship with the hydrolysis constants of the metals when plotted on a log-scale. Therefore each mineral has its own LFER with a characteristic intercept and slope which is supported in the literature for several minerals.

Site-specific data for Am, Eu and Ni sorption to Forsmark metagranite in saline and fresh groundwater were used to evaluate the LFER approach. The results calculated to predict sorption of radionuclide species in the fresh Forsmark groundwater showed good agreement with the experimental data. The proposed approach appears to be a promising method for making predictions with sparse measurement data. It will be evaluated further using site specific data from Laxemar and Äspö Hard Rock Laboratory. In addition, insights obtained during the work involving a generalised composite modelling approach suggest some simplifications for modelling of surface complexation involving pure mineral phases. The complete description of those activities can be found in the S&T contributions Crawford (2012, 2013).

WP5: Application to the safety case

WP leader:

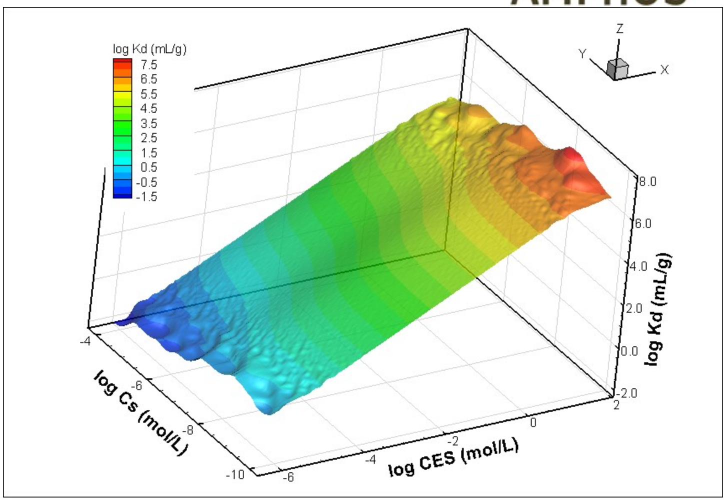
Jorge Molinero

Amphos 21

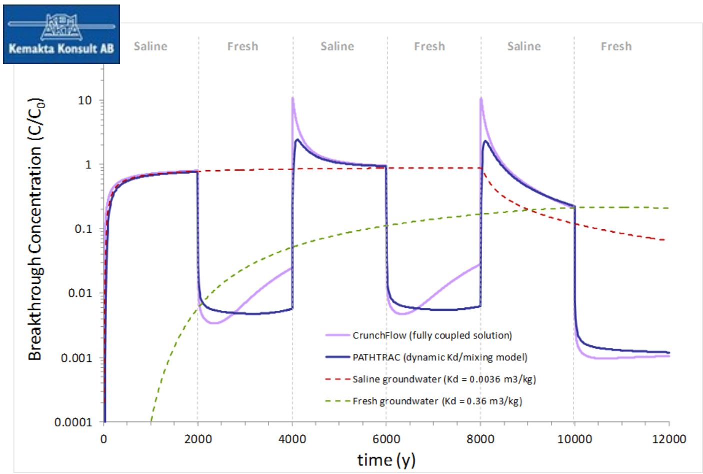
The work of this WP has focused on assessing different modelling approaches that, on the one hand allow nonlinearities to be properly accounted for and, on the other hand, try to circumvent the computational limitations of “standard” fully coupled models.

Three organizations form this WP: Amphos 21 (Spain), KEMAKTA (Sweden) and VTT (Finland). Two deliverables, D5.1 and D5.2, were generated within this WP. Below, a few details of the activities carried on by the different organizations involved in this WP are provided.

Different methodologies have been tested against a synthetic benchmark exercise that describes the migration of a set of radionuclides from the repository to the surface. A so called, FASTREACT methodology, was used to carry out mechanistic reactive transport simulations. The results of the simulations have shown that, when matrix diffusion is neglected, the breakthrough curves of the considered radionuclides (i.e. Sr, Ra and Cs) reflect the distribution of the ensemble of trajectories with a sharp arrival peak followed by a fast decrease of concentration. Further details of this work can be found in the S&T contributions Trinchero et al. (2012, 2013).



Results of the Monte Carlo simulation: cesium distribution coefficient (K_d) as a function of the aqueous concentration of cesium and the number of exchange sites (CES).



Comparison of breakthrough curves for Ra^{2+} migration simulated using PATHTRAC and a fully coupled reactive transport simulation using CrunchFlow for the temporally variable boundary conditions (as indicated by the fresh/saline labelled intervals in the figure). Breakthrough data are normalised relative to the constant inlet concentration boundary condition (10^{-12} mol/kgw).

In parallel, the CrunchFlow program was used to reproduce the breakthrough curves for the cation exchanging solutes obtained previously using the simplified modelling approach incorporated in the PATHTRAC program. It was found that although remobilization of cation exchanging radionuclides could be modelled approximately using the decoupled major ion chemistry modelling approach, the breakthrough curves did not fully match those of the fully coupled simulations. A complete description of this exercises is provided in the S&T contributions Crawford (2012, 2013).

WP leader:

Jorge Molinero

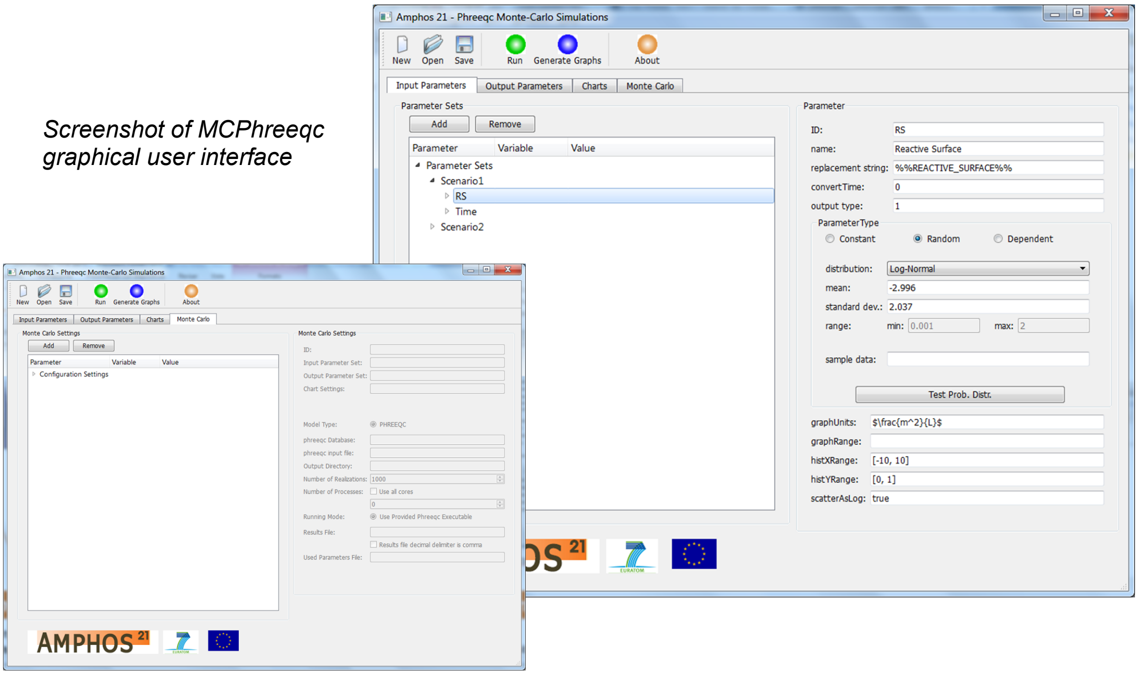
Amphos 21

WP5: Application to the safety case

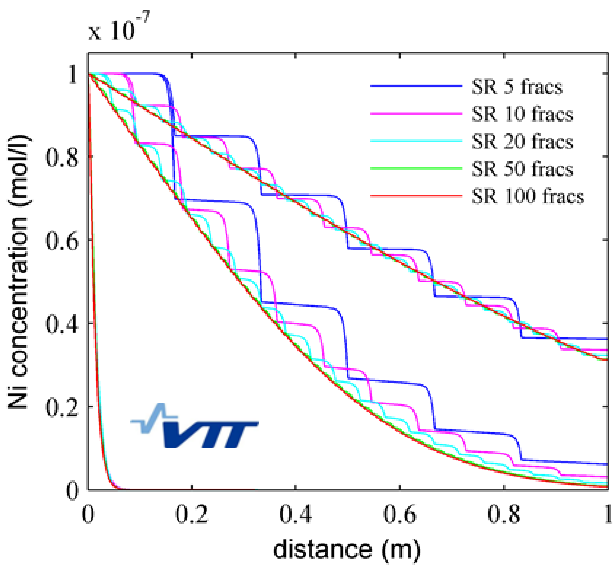
The aforementioned numerical exercises have demonstrated the great potentiality of a number of “new” methodological approaches that, allowing non-linearities to be explicitly and efficiently accounted for, could help in reducing the intrinsic conservatism of safety assessment calculations.

Nevertheless, in these type of applications one has always to deal with the epistemicity related to the different processes and the related variables. Thus, a rigorous stochastic framework is needed to quantify the uncertainty associated to the results of the calculations. To this end, in the framework of this WP, a tool, denoted as MCPhreeqc, has been developed to apply Monte Carlo simulations automatically to the PHREEQC geochemical models

Screenshot of MCPhreeqc graphical user interface



Additionally, an analysis on how reactive transport modelling can support PA exercises in fractured bedrock was performed. Closely related with this, modelling of Ni reactive transport in fractured media was studied. Three different reaction models for sorption of nickel on biotite were coupled to a fracture flow model. The three models show somewhat similar sorption behaviour in the case of sorption of nickel and biotite, but give insight into interpreting experimental results for PA models. Additional details are available in the S&T contributions by Olin et al. (2013) and Pulkkanen et al. (2013).



Soluble Ni^{2+} concentration profile at the midline of the fracture at times 0 years (lowest set of lines), 0.2 years (middle) and 1 year (top).

WP6: Documentation

WP leader:

Andrés Idiart

Amphos 21

This WP focused on the review of those processes which exert a major influence on the transport and retention of radionuclides in the far-field, as well as on the main conceptual models describing these processes available in the scientific literature.

Amphos led this WP, with the contribution of all the project members. Based on the results of a questionnaire distributed among different international organisations, an analysis was conducted of how these retention processes are taken into account and modelled in the different Performance Assessments (PAs) currently being carried out by radioactive waste management organisations. The focus was on the evaluation of the long-term safety of deep geological disposal facilities for radioactive waste in crystalline rocks. The results have pointed out a number of issues in the PA that need further treatment with regards to transport and retention processes and having potentially high impact on radionuclide transport in the geosphere including:

- Bentonite erosion and formation of colloids as a result of intrusion of low-salinity waters into the near-field.
- Mixing and dilution during advective transport.
- Radionuclide re-mobilization.
- The effect of degradation of cementitious materials due to interactions with groundwater: the formation of hyper-alkaline plume and its impact on physical and chemical properties of the affected rock.
- Microbial activity. In particular microbial-mediated remobilization processes that may be characterized by slow kinetics.
- Modelling of solute transport: PA exercises could be improved by considering more detailed transport models than the simple models currently used.

Most experts agree that the main challenges in modelling of radionuclide transport within Performance Assessment lie in the areas of:

- Sufficient conceptual understanding of relevant processes that control the transport and retention of radionuclides
- Adequate implementation of conceptual models into Performance Assessment codes
- Acquisition of reliable data for model parameterization

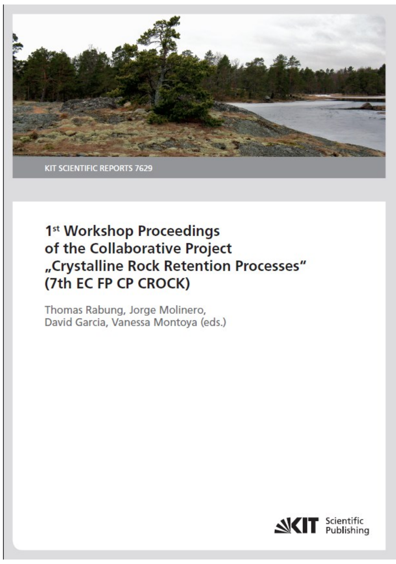
More details can be found in the S&T contributions Idiart et al. (2012, 2013) and the Workshop presentations available on the CROCK webpage (www.crockproject.eu).

WP7: Knowledge management, dissemination and training

WP leader:

David García

Amphos 21



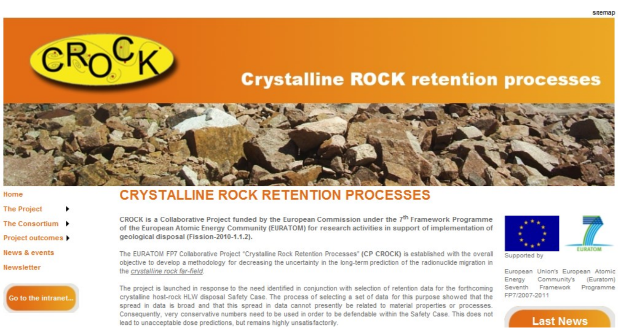
1st CP CROCK Workshop Proceedings front page

Knowledge management and dissemination activities included within WP7 were:

- To establish the project web portal (www.crockproject.eu) at the beginning of the project.
- To prepare the project presentation. This document was published in the brochure of project synopses funded by **EURATOM F**ission FP7.
- To generate the generic poster of the project. The poster has been presented at several conferences e.g. the 13th and 14th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (MIGRATION'11 and MIGRATION'13), held in Beijing, China in September 2011 and in Brighton, UK on September 2013, EuCheMS International Conference on Nuclear and Radiochemistry (NRC-8) – held in Como, Italy in September 2012 and the EURADISS conference held in Montpellier, France in October, 2012
- To prepare three newsletters informing about the project latest progress
- Edition of two Workshop Proceedings, for the first and the second **(and Final)** project Workshops. Proceedings have been generated and published as KIT Scientific Reports and are available for downloading from the project website.

The training program have been included in the 1st and 2nd Annual Workshop of the project (May, 22nd - 24th, 2012 and May 14th - 16th 2013) as Topical Sessions. The topics covered in these sessions have been "Reactive transport modelling" and "In-situ URL experiments", respectively, where different presentations during the first day of the workshops have been given by beneficiaries and external experts. Documentation of the Topical Sessions is included in the project webpage (www.crockproject.eu).

Project website home (www.crockproject.eu



Beneficiaries:

Conterra AB

EUG members:

Events

The *Final CP CROCK Workshop* was held in Karlsruhe (Germany), in May 2013. The workshop was organized by KIT-INE (www.ine.kit.edu).

The main focus of the workshop was to present and discuss the scientific and technical outcomes of the project. The workshop was structured in several plenary sessions. A poster session was also organized as a training action for the younger scientist.

In association with the Final Workshop, a Topical Session on “In situ URL experiments” was organized.

Additionally, it is worth to mention that results gathered within the CROCK project will be presented in the forthcoming conferences:

- Goldschmidt 2013, Florence (Italy) August 2013.
- Migration 2013- 14th International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the geosphere, Brighton (UK) September 2013.
- EURADWASTE’13, Vilnius (Lithuania) October 2013